# Quantitative Chemical Mass Transfer in Coastal Sediments During Early Diagenesis: Effects of Biological Transport, Mineralogy, and Fabric-Phase III

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## LONG-TERM GOALS

Our long term goals are to provide a better quantitative and mechanistic understanding of chemical processes that occur in fine-grained coastal and continental margin marine sediments, especially with regard to how these processes affect biogeochemical fluxes and the transport and/or retention of environmentally sensitive natural and anthropogenically generated chemical compounds in coastal environments.

## **OBJECTIVES**

The objective of this project is to make better predictions of chemical mass transfer in fine-grained siliciclastic coastal sediments, especially with regard to the impact of biologically-enhanced transport and the effects of sediment mineralogy, fabric, and particle surface chemistry on the fluxes of biochemical species and pollutants in coastal marine sediments. Production of a computer code is a prime objective.

#### APPROACH

Our approach combines the strengths of investigators from three institutions, Scripps Institution of Oceanography (SIO), The Naval Research Laboratory at the Stennis Space Center (NRL), and Georgia Technological University (GTU). This consortium is working together to integrate controlled laboratory experiments on chemical transport processes in model sediments (SIO) with field-based biogeochemical studies and sediment fabric/microfabric characterizations (NRL) and numerical reactive transport modeling (GTU). The overall objectives for the SIO team in this time period are to determine mechanisms of mineral-bio-organic interactions in fine-grained siliciclastic sediments with results to be used to upgrade STEADYSED, a multicomponent numerical model of reactive transport in aquatic sediments.

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Form Approved OMB No. 0704-0188 The SIO team is accomplishing its goals of uncoupling sediment-mineral-microorganism through a program of studies using model sediments and reactors. The program focuses in determining mechanisms of interaction and understanding the dependence of sediment permeability, porosity and fabric on (1) organic matter and microbial populations associated with mineral surfaces, (2) mineralogy and (3) burrowing activity of macrofauna. Results of these studies are in the process of being incorporated into STEADYSED our consortium's existing reactive transport model of early diagenesis.

#### WORK COMPLETED

The reactor prototype is completed and now being modified to permit time-series sampling of pore fluids using osmotic pumps. Five, end member, sediment mixtures have been established that represent high latitude (chlorite-rich), mid-latitude (illite-rich), and Mississippi Gulf Coast (smectite-illite-rich) fine-grained coastal sediments. Initial water retention studies of the model sediments are complete and the chemical and surface characterization of pure minerals and mineral mixtures are near completion. Preliminary embedding trials of the model sediments, as well as model sediments that have been colonized by microorganisms are underway in preparation for TEM microfabric analysis.

Conductivity studies of model sediments for use in Phase III reactor experiments for determining the effects of clay mineralogy on sediment formation factor (i.e., permeability proxy) are underway. Experiments to determine whether organic compounds dissolved in seawater have a preference for different minerals are complete with adsorption experiments focusing on minerals (or their proxies) to be used in the reactor experiments. Analyses of surface coverage, organic chemistry, and chemical bonding are underway in outside laboratories.

Algorithms and tables for correcting sediment porosity for the presence of organic matter were published. Mechanistic interactions between minerals, microbes, and organic matter in fine-grained siliciclastic sediments, that are consistent with data from previous ONR-funded TEM microfabric studies, were published. Osmotic samplers for the time-series sampling of sediment porewaters were designed and built (with H. Jannasch, Monterrey Bay Aquarium Research Institute) and the technique published. A general model for microfabric-induced preservation of organic matter is in progress, as is an analysis the influence of SIO porosity corrections on calculated biogeochemical fluxes.

#### RESULTS

Water retention studies of our model sediments, in preparation for their use in the reactor systems, show that chlorite-rich sediments have significantly less porosity than do those with illite, kaolinite, and montmorillonite-rich mixtures. This difference is on the order to 5-10%. This work also indicates that as silt content increases the influence of the clay mineral suite decreases dramatically.

Initial investigations into sediment conductivity show distinct difference in behavior between pure kaolinite, illite, and montmorillonite. Porewaters of low ionic strength show a strong electrical response to the clay mineral surfaces, with montmorillonite showing the largest effect. As ionic strength increases to seawater values, this effect decreases dramatically.

Osmotic samplers using salt gradients and membranes calibrated for medical purposes have been successfully engineered into osmotic sampling devices that make possible high resolution time-series

sampling of marine sediment porewaters. Porewaters are drawn through osmotic processes up into long capillary tubes, initially filled with distilled water. Porewaters displace the distilled water. To sample, capillary tubes are crimped into lengths that provide the resolution and amount of solution required for the objectives of a particular study.

Our analysis shows that the bacterial habitation of marine sediments significantly affects the evolution of sediment physical properties and is a potential major influence on fine-grained sediment chemical transport. Almost without exception, the external surfaces of the bacteria are covered with secreted exocellular slimes composed of cross-linked polysaccharide fibrils. These fibrils act to bind sediment grains into relatively robust microaggregates which can significantly impact the interaction between microbes and minerals, as well as the chemical and physical transport of fluids and dissolved aqueous species through the sediment.

## IMPACT/APPLICATION

The conductivity studies on fine-grained sediments, when complete, provide the first quantitative data on the dependence of sediment resistivity on clay mineral mixtures. This provides better estimates of the formation factor which is a key parameter in equations for calculating geochemical fluxes as a proxy for the transport properties of the sediment. This should lead to more quantitiave calculations of chemical fluxes for important chemical species that move along concentration gradients out of the sediment and into the water column.

The organic matter adsorption studies, for the first time will demonstrate, using direct measurements, whether there are compound-specific interactions that control the clases of organic compounds associated with the surfaces of different minerals, expecially clay minerals, in coastal marine sediments. This has implications for the preservation of organic carbon in sediments, as well as the sites in sediments where organic pollutants might tend to concentrate.

## **TRANSITIONS**

Model sediments developed in this project are being used by Dr. Bradley Tebo and his research group at the Scripps Institution of Oceanography to determine the specificity of bacterial consortia for sediments comprised of different clay mineral suites.

Samples of sediments taken from preliminary water content studies are being used by Dr. Richard Bennett of SeaProbe, an ONR contractor, to use high resolution imaging techniques to study mineralogical effects on sediment texture.

#### **PUBLICATIONS**

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